FABRICATION OF NF MEMBRANE USING PHASE INVERSION METHOD FOR DYE REMOVAL

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ABSTRACT

Nowadays membranes play an important role as a separation tool in many industrial processes such as in pharmaceutical and biotechnological industries, in pure water production and in water and waste water treatment. Rejection of dye concentration one of the factors that can reduce the performance of membrane as well as flux decline and indirectly will affect the quality of the water produced and consequently increases in cost and energy replacement. The rejection can define as the percentage of solids concentration removed from system feed water. Therefore this research was conducted to produce high performance of NF membrane by manipulating the concentration of PES in order to produce the high rejection of colour removal. The manipulated variable is the percentage concentration of PES, meanwhile the dependent variable is percentage PVP and also NMP. In this study, the membranes were synthesized by using wet phase inversion method. In this method, the cast polymer solution is immersed in water bath and absorption of water will cause the film to rapidly precipitate from the top surface of membrane. Based from the 3 membrane that studied which is 18% PES membrane, 20% PES membrane, 23% PES membrane, 23% PES membrane gives greatest rejection 64.64% at 3 bar pressures applied. In the meantime, the value of flux at high percentage concentration of PES decrease 16.0162 L/m^2.h compare with low percentage PES concentration 871.0801 L/m^2.h. This is due to the thickness and tightens the porosity at high percentage concentration of PES. Increased feed water pressure also results in increased the dye rejection.

ABSTRAK

Kini membran memainkan peranan penting sebagai alat pemisahan dalam proses industri seperti industri farmaseutikal dan bioteknologi, dalam pengeluaran air tulen dan air dan rawatan air sisa. Penolakan kepekatan warna salah satu factor-faktor yang boleh mengurangkan prestasi membran serta penurunan flux dan secara tidak langsung akan menjejaskan kualiti air yang dihasilkan dan seterusnya meningkatkan kos dan penggantian tenaga. Penolakan itu boleh ditakrifkan sebagai peratusan kepekatan pepejal yang dikeluarkan dari sistem air aliran masuk. Oleh itu, kajian ini dijalankan untuk menghasilkan prestasi yang tinggi membran NF dengan memanipulasi kepekatan PES untuk menghasilakn penolakan penyingkiran warna yang tinggi. Pemboleh ubah yang dimanipulasikan adalah kepekatan PES untuk menghasilkan penolakan penyingkiran warna yang tinggi. Pemboleh ubah bersandar pula adalah peratusan PVP dan NMP. Dalam kajian ini, larutan cast polimer direndam di dalam air rendaman dan penyerapan air akan menyebabkan lapisan nipis (filem) dengan pantas termendak dari permukaan atas membran. Berdasarkan dari tiga membrane yang dikaji yang membrane PES 18%, 20% membrane PES, 23 % membrane PES, 23% membrane PES memberikan penolakan terbesar 64.64% pada tekanan 3 bar yang digunakan. Pada masa yang sama, nilai flux pada peratus kepekatan PES yang paling tiggi berkurang 16.0162 $L/m^2.h$ berbanding dengan peratusan rendah peratusan kepekatan 871.0801 $L/m^2.h$. Ini adalah kerana ketebalan dan ketetatan liang pada kepekatan peratusan tinggi PES. Tekanan aliran air masuk yang meningkat juga menyebabkan peningkatan penolakan warna yang tiggi.

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LIST OF ABBREVIATION

MB	Methylene blue
NF	Nanofiltration
NMP	1-methyl-2-pyrrolidone
PES	Polyetehersulfone
PVP	Polyvinylpyrrolidone
RO	Reverse osmosis
UF	Ultrafiltration

CHAPTER 1

INTRODUCTION

This chapter will introduce about the topic of research method and also goal of this study. Besides that, this chapter also will describe about process of clarifying the scopes of the study and identifying the problem statement. It also will cover about the significant of this study to the environment and to the human being as well.

1.1 Research background

In chemical process industry, separation processes are crucial as chemical reaction and high purity water is necessary. Azhar and Liew (2005) observed that recently it was guesstimate that over 7 x10^5 tonnes of 10 000 commercial dyes and pigments exist and produces annually world wide. These dyes are hardly fading on exposure water, light and many chemical due to their complex chemical structure and synthetic origin. The industry such as printing, textile, paper, plastic, cosmetic and other else are needed to recovery the dyes for their manufacturing and treatment process. Azhar and Liew (2005) also confirmed that textile industry is the first rank in usage of dyes for coloration of fibre among these industries.

This dyes effluent should be treated as it may exert great impact to our mother earth as well as to our health. In order to reduce or prevent the effluent dyes, many researches have been conducted to find the most effective and economical ways to treat this effluent. There are several methods of dyes removal from industrial effluent which is can be characterized into two parts which is physical and chemical method. Gonder et. al., (2010) have reported that among the advanced treatment processes, membrane technology offers an attractive alternative method to treat dye effluent for that purposed as well as its consume less energy, low space requirement and also simplicity of operation (Celik et al.,2010).

Nowadays, more and more field is planning to use membrane technology to separate the fluid and get high quality result. The application of membrane separation process are expending much larger with the principal of the membrane technology as it is also bring significant economy benefits. Recently many countries in the world have noticed the crucial of membrane technology especially deficient in resources, short of energy and also declining environment is all in existence in our life. Thus, the industries and the technology regard the membrane separation technology is very important in our daily life.

Membrane act as a semi permeable barrier and separation occur by the membrane controlling the rate of movement of the various molecules between two liquid phases. There basically have three type of membrane which is ultrafiltration (UF) membrane, reverse osmosis (RO) membrane and also nanofiltration (NF) membrane. Petrinic et. al., (2007) studies' show that, the UF membrane could not completely decolourise wastewater as it did not remove low molecular weight dyes.

Meanwhile to assure the decolourised and desalinated of wastewater the combination of RO and NF is required. This is due to the behaviour of RO itself can desalinate (NaCl retention) wastewater effectively up to 93% beside produce a colourless permeate. But this research focusing more on decolourised of divalent ion and dye molecules only. Petrinic et. al., (2007) also observed that the NF show it can remove up to 99% of dyes and 84% electrolyte even sodium chloride can pass trough it. So, that direct NF of dye water is the most realistic method for the dye removal treatment.

1.2 Problem statement

The most important goals in membrane technology are to control the membrane structure and thus the membrane flux and rejection. Even NF show that the dye can remove up to 99%, but not all type of dye can exactly remove until 99%. Therefore this research was conducted to know how much the dye of MB will reject via phase inversion method by manipulation of PES concentration

1.3 Objective

The main objective of this research is to produce high performance of NF membrane by using phase inversion method and also to produce high rejection of the NF membrane by manipulating the concentration of PVP and PES.

1.4 Scope of study

In order to meet the objective, there are some scopes that need to be focused:

i. To fabricate NF membrane by using phase inversion method

ii. To study the effect of PES concentration on NF performance (flux, dye removal and percentage rejection)

1.5 Significance of study

There have so many significance of this research in term of knowledge generation and positive social change that would be beneficial not only to the human community and culture but also to the environment. Firstly, the priority doing this research is to remove the colour from the effluent of textile industry since Azhar and Liew (2005) have reported that textile industry is the first rank in usage of dyes for coloration of fibre among these industries. Because the huge consumption of dye in this industry, dye removal is so important in order to be friendly to our mother nature.

Beside, Gonder et. al., (2010) have stated that the high consumption of fresh water is the most crucial environmental concern in the industry. Thus, in order to reduce the consumption of freshwater and lower the wastewater treatment plant capacity, there is a need to recycle the treated wastewater. The cost of treatment this water effluent also reduced since the membrane filtration are the more cost effectively compare to others (Ali et. al., 2009)

Other than that, the significant of this study is to follow the standard quality of Environmental Quality Act 1974 [Act 127]. In this Act 127, there have stated the limit of dye of effluent can be discharge for Standard A is 100 ADMI (American Dye Manufacturer Institute) and Standard B is 200 ADMI. For the Standard A, the catchment areas referred to the areas upstream or surface above subsurface including water intakes which are the water for the human consumption including drinking. Meanwhile for the Standard B is for the any other inland waters not including human consumption.

CHAPTER 2

LITERATURE REVIEW

This chapter will point out about the definition and the basic concept of membrane separation technology, membrane structure that have been used nowadays and also the membrane module in separation industry.

2.1 Membrane definition

Membrane can be defined basically as thin layer of semi-permeable barrier, which separate two phases and restrict transport of various chemical when a driving force is applied across the membrane (G. Srikath, 2011). It can control the rate of movement of various chemical between two liquid phases, two gas phase, or a gas and liquid phases. The chemical component that allowed passage by the membrane into the permeate stream is called permeate, whereas the others that retain and accumulate is known as retentate. The two fluid phases are usually miscible and the membrane barrier prevents actual, ordinary hydrodynamic flow. A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure, solid or liquid. This membrane process are increasingly used nowadays for removal of bacteria, microorganism, particulates, and natural organic material, which can impart colour, tastes, and odours to water and react with disinfectants to form disinfection by product.

2.2 Principle of membrane based separation process

There are two ways for membrane separation process which is dead end filtration and cross flow filtration as shown in Figure 2.1.

2.2.1 Dead End Filtration

In the dead end filtration, the pressure will apply to the feed solution as a force through the membrane. The surface of the filtration membrane is vertical with the feed flow direction. Basically the filtrate direction which passes the membrane is the same direction with the feed flow. The particles that retained in the feed solution will adhere to the surface of membrane which causes clogged and the consequently cartridge filters have to be replacing frequently and can not reused to maintain the performance of membrane.

2.2.2 Tangential (Cross) Flow Filtration

In the cross flow filtration, the fluid to be separated is pumped across the membrane parallel to its surface. Clear permeate and retentate solution that containing most of the retain particle in the solution will produce from the cross flow. The retained particle can be swept off the membrane surface by maintaining a high velocity. This will make the cross flow filtration is more efficient in operation compare to dead end filtration that easily built up the filter cake

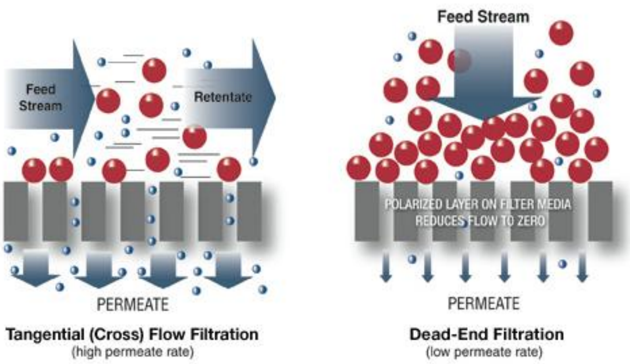

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Figure 2.1: Membrane separation process (Schmeling et.al, 2010)

2.3 Membrane structure

The proper choice of membrane should be determined by their specific application. There are two type of membrane structure that commonly used which is asymmetric and isotropic membrane. The different between these two structures are the physical and chemical properties.

2.3.1 Asymmetric Membranes

Asymmetric or as known as anisotropic are non-uniform over the membrane cross section and they consist of a number of layers each with different structure permeability and chemical composition. The skin layer is very thin (0.1- 1.0 micron) and highly porous (100-200 microns) thick substructure (G. Srikath, 2011). Chakrabarty et.al, (2008) stated this membrane are characterized by the existence of a dense top layer and a porous sublayer. Because the nature of this membrane itself have a thin top layer that acts as a selective barrier film, and a porous sublayer that offer good mechanical strange makes this membrane have been widely used for gas and liquid separation process.

2.3.2 Isotropic membrane

2.3.2.1 Nonporous membrane.

The transmembrane of dense nonporous isotropic membrane fluxes through this membrane relatively thick make it to low for practical separation process and rarely used in membrane separation process. On the other hand, this nonporous isotropic membrane is commonly used in laboratory work to characterize the membrane properties.

2.3.2.2 Microporous membrane.

This isotropic microporous membrane almost behave like fibre filter and separate by sieving mechanism determined by the pore diameter and particle size. The pores in the membrane may vary between 1nm- 20 micron (G. Srikath, 2011). By comparing with the isotropic dense membrane, the isotropic microporous membranes have higher fluxes and more widely used as microfiltration membrane. Besides, it is also used as a inert spacers in a battery and fuel cell applications and as the rate controlling element in controlled drug delivery device.

2.4 Type of membrane separation process

There are various types of membrane separation that have been developed for specific application. Each of those have different characteristic and some are widely used in industry. This membrane separation process to be considered here is a membrane liquid process such as reverse osmosis, ultrafiltration, microfiltration and nanofiltration. The difference between these four membranes has shown in Table 2.1 below.

Table 2.1: Comparing Four Membrane Process (Wagner. J, 2001)

	Reverse Osmosis	Nanofiltration	Ultrafiltration	Micro filtration
Membrane	Asymmetrical	Asymmetrical	Asymmetrical	Symmetrical Asymmetrical
Thickness Thin film	150 μm 1 μm	150 μm 1 μm	150 - 250 μm 1 μm	10-150 μm
Pore size	<0.002 μm	<0.002 μm	0.2 - 0.02 μm	4 - 0.02 μm
Rejection of	HMWC, LMWC sodium chloride glucose amino acids	HMWC mono-, di- and oligosaccharides polyvalent neg. ions,	Macro molecules, proteins, polysaccharides vira	Particles, clay bacteria
Membrane material(s)	CA Thin film	CA Thin film	Ceramic PSO, PVDF, CA Thin film	Ceramic PP, PSO, PVDF
Membrane Module	Tubular, spiral wound, plate-and-frame	Tubular, spiral wound, plate-and-frame	Tubular, hollow fiber, spiral wound, plate-and-frame	Tubular, hollow fiber
Operating pressure	15-150 bar	5-35 bar	1-10 bar	<2 bar

2.4.1 Reverse osmosis membrane

Reverse osmosis (RO) is the tightest possible membrane process in liquid-liquid separation. The process RO membrane just not only can remove some suspended solid but also it does eliminate bacteria, viruses and other germ that contain in water (G. Srikath, 2011). RO is essentially a pressure driven membrane diffusion process for separating dissolve solute. According to Geankoplis (2003) the important commercial used of RO is in the desalination of seawater or brackish water because of the effectiveness and characteristic of RO itself. Reverse osmosis membranes have the smallest pore structure, with pore diameter ranging from approximately 5-15 A^{o} (0.5 nm - 1.5 nm). The operating pressures in RO are generally between 10 and 100 bar (J. Timer, 2001). Extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semi-permeable membrane along with the water.

2.4.2 Ultrafiltration membrane

UF is a membrane process that is quite comparable to reverse osmosis. It is a pressure driven process where the small solute molecule pass thought the membrane and are collected as a permeated. Basically, the solute or molecules to be separate have a higher molecular weight which is greater than 500 and up to 1000 000 or more such as polymers, starch and etc (Geankoplis, 2003). The UF membrane has small pore diameters size, between 10Å to 2000Å.

2.4.3 Microfiltration membrane

The separation of micron and submicron level can be efficiently be operate by using microfiltration membrane filter. The pore sizes of microfiltration membranes are usually larger than RO, UF and NF. Microfiltration membrane are used to filter the size particle that have range from 0.02 µm to 10 µm such as suspended particulate, bacteria or large colloids from solutions. This membrane usually used the pressure from 100kPa to 500kPa.

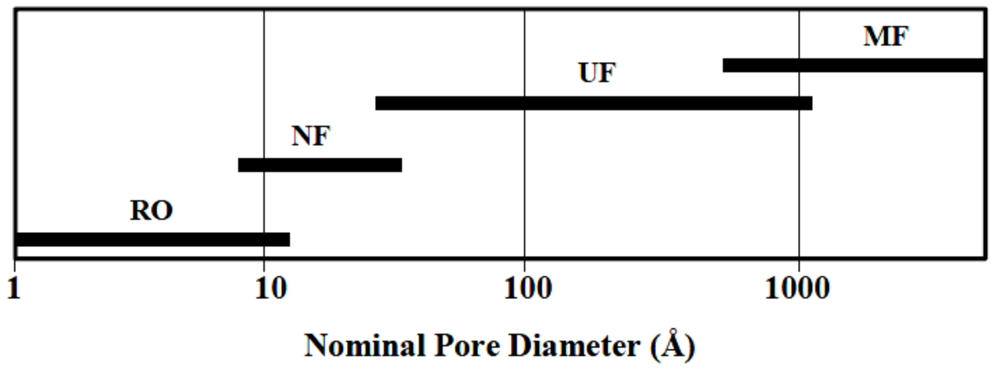

Figure 2.2: Range of membrane nominal pore size (Sagle, A & Freeman, B)

2.4.4 Nanofiltration membrane

Nanofiltration membrane is the most recent membrane that is very thin and has a small pore size which is between 10nm to 200nm. The pressure that used in nanofiltration process is from 0.3 MPa to 3 MPa. This membrane is known as different from others because it consist charge and can reject ion with more than one negative charge, such as sulphate or phosphate, while passing single charge ion. This charge is basically used to retain selective molecule to avoid fouling (Cheng et.al, 2010). Wagner. J (2001) comment that NF also rejects uncharged, dissolved materials and positively charged ions according to the size and shape of molecule in the solution and also feed concentration.

2.5 Membrane module

A membrane module is a pack of the membrane area into the least volume, to decline the capital and operating cost with providing acceptable flow hydrodynamics in the vessel. The practicability of the membrane separation process usually depends on the module configuration as the active separation membrane area can affect the membrane module configuration. There are four type of membrane which is tubular, spiral wound, plate and frame and hollow fibres. The comparison between these four membranes has been discussed in Table 2.2.

2.5.1 Tubular

The tubular module are now generally restricted to ultra-filtration, for which the benefit of resistance to membrane fouling outweighs the high cost. These modules enclose as many as 5 to 7 smaller tubes, each 0.5 to 1.0 cm in diameter (Cheah S M., 2000). The membrane is often on the inside of a tube and the feed solution is pumped through the tube and permeate is removed from each tube from each tube and sent to permeate collection header.

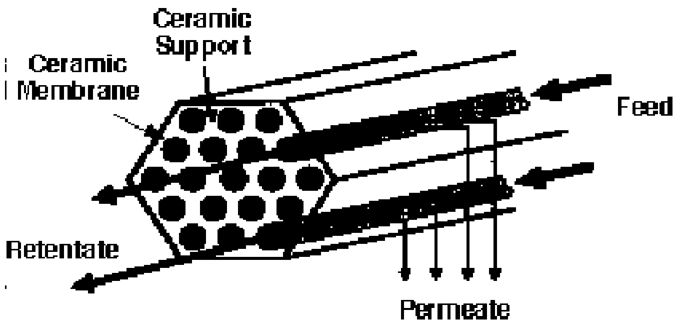

Figure 2.3:A schematic drawing of a tubular membrane module(Sagle,A& Freeman, B)

2.5.2 Spiral wound

The spiral wound module very popular in industry for nanofiltration or reverse osmosis membrane. This module has a flat sheet membrane wrapped around a perforated permeate collection tube. The feed flows on one side of the membrane and permeate is collected on the other side of the membrane meanwhile spirals in towards the centre collection tube. The low price and very compact design of spiral wound module was originally made exclusively for water desalination caught the attention to other industry (Wagner.J, 2001). But nowadays after redesign have made, this module can be used for a variety of industrial application such as in the dairy industry, the pulp and paper industry and other else.

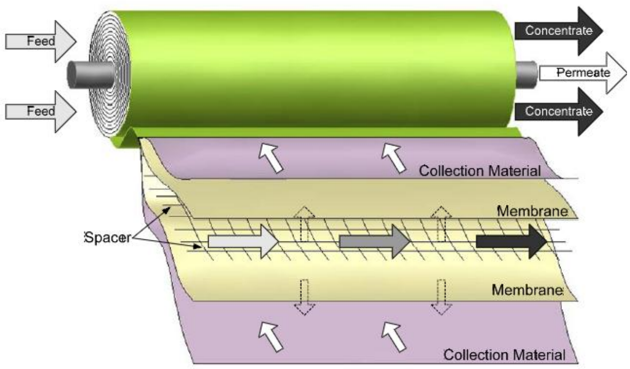

Figure 2.4: A schematic drawing of a spiral wound membrane module (Li et al., 2006).

2.5.3 Plate and Frame

Plat and frame membrane module were one of the earliest type of membrane modules and were widely used in separation process. But, because of their relatively high cost they have replace in most application by spiral wound modules and also hollow fiber modules. Nowadays, the plate frame module used only in electrodialysis and pervaporation system in a limited number of reverse osmosis and ultrafiltration applications with highly fouling condition (Cheah S M., 2000).

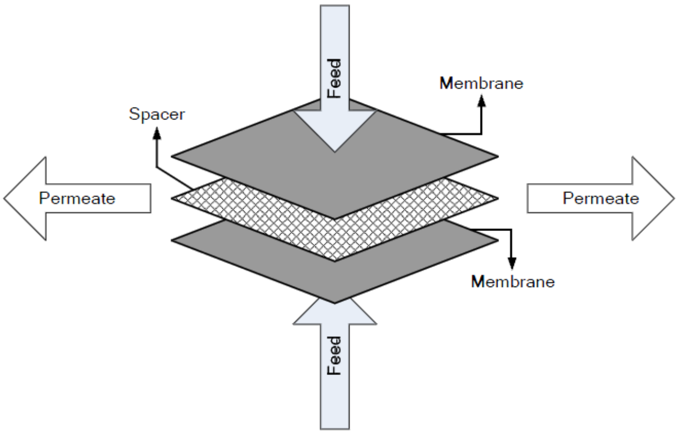

Figure 2.5: A schematic drawing of a plate and frame membrane module (Li et al., 2011).

2.5.4 Hollow Fibres

The hollow fiber module also has been widely used for desalination that usually consists of bundle of hollow fibers in a pressure vessel. The figure 2.6 below depicted a schematic drawing two kind of a tubular membrane module based on different operation condition. This module has been characterized in 4-8 inch (10-20 cm) in diameter and 3-5 feet (1.0-1.6 m) long (Cheah S M., 2000). The system of hollow fiber module will pressurised from the shell side, and the filtrate passes pass along the fibre wall and exits through the open fibre ends. Bore-side of hollow fiber modules can also be used where the feed is circulated through the fiber. The most advantages of hollow fiber modules are the ability to pack a very large membrane to single module. For instance, in an 8-inch diameter, 40-inch long spiral-wound module would contain about 20 - 40 m^2 of membrane area. The correspondent hollow-fibre module filled with fibres of 100-mm diameter will contain approximately 600 m^2 of membrane area.

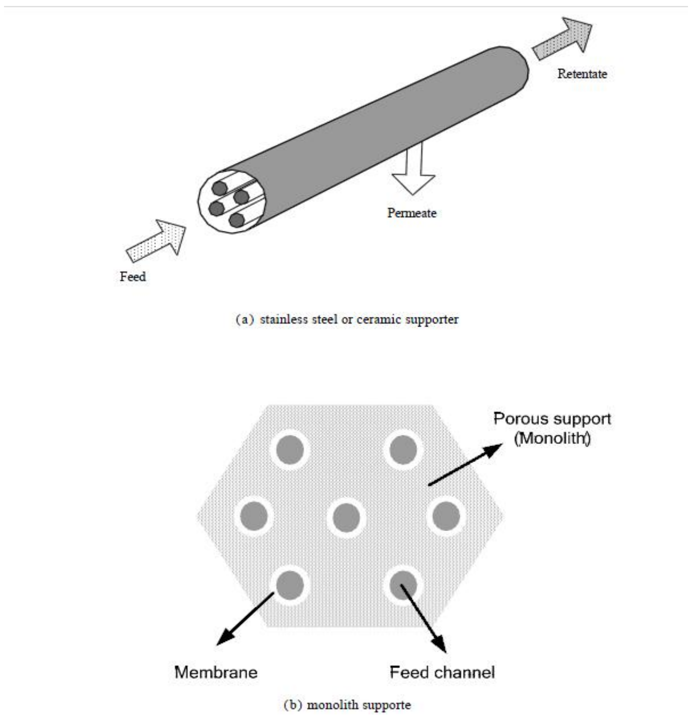

Figure 2.6: A schematic drawing of a tubular membrane module (Li et al., 2011).